

High-resolution inelastic X-ray scattering studies of the state-resolved differential cross-section of Compton excitations in helium atoms

B. P. Xie,¹ L. F. Zhu,^{2,*} K. Yang,^{1,†} B. Zhou,¹ N. Hiraoka,³
Y. Q. Cai,^{3,‡} Y. Yao,⁴ C. Q. Wu,⁴ E. L. Wang,² and D. L. Feng^{1,§}

¹*Department of Physics, Surface Physics Laboratory (National Key Laboratory), and Advanced Materials Laboratory, Fudan University, Shanghai 200433, P. R. China*

²*Hefei National Laboratory for Physical Sciences at Microscale, Department of Modern Physics, University of Science and Technology of China, Hefei, Anhui, 230026, P. R. China*

³*National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan, Republic of China*

⁴*Department of Physics, Fudan University, Shanghai 200433, P. R. China*

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Abstract

The state-resolved differential cross sections for both the $1s^2 \ ^1S_0 \rightarrow 1s2s \ ^1S_0$ monopolar transition and the $1s^2 \ ^1S_0 \rightarrow 1s2p \ ^1P_1$ dipolar transition of atomic helium have been measured over a large momentum transfer region by the high-resolution inelastic X-ray scattering (IXS) for the first time. The almost perfect match of the present measurement with the theoretical calculations gives a stringent test of the theoretical method and the calculated wavefunctions. Our results demonstrate that high-resolution IXS is a powerful tool for studying the excitations in atoms and molecules.

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*Electronic address: lfzhu@ustc.edu.cn

†Present affiliation: Shanghai institute of applied physics, Chinese Academy of Sciences. P. R. China.

‡Present affiliation: NSLS-II, Brookhaven National Laboratory, USA.

§Electronic address: dlfeng@fudan.edu.cn

After the discovery of Compton effect in 1923, it was soon recognized that Compton effect can give valuable information about the electronic momentum density of the target [1]. About forty years later, Platzman and coworkers found that the Compton profile measured by the cross section of the Compton ionization, gives information on the electron momentum distribution of the ground state; while the Compton excitation measured through inelastic X-ray scattering (IXS) or X-ray Raman scattering, can be used to probe the wavefunctions of electrons in excited state [2]. The differential cross section (DCS) of Compton excitation can be described by:

$$\frac{d^2\sigma}{d\Omega d\omega_f} = r_0^2 \frac{\omega_f}{\omega_i} |\vec{\epsilon}_i \cdot \vec{\epsilon}_f^*|^2 S(\vec{q}, \omega),$$

where $S(\vec{q}, \omega)$ is the dynamical structure factor defined as

$$S(\vec{q}, \omega) = \sum_f |\langle \psi_f | e^{-i\vec{q} \cdot \vec{r}} | \psi_i \rangle|^2 \delta(E_i - E_f + \hbar(\omega_i - \omega_f)),$$

$\omega = \omega_i - \omega_f$ is the energy loss, and $\vec{q} = \vec{k}_i - \vec{k}_f$ is the scattering vector. $S(\vec{q}, \omega)$ provides a more comprehensive description of the excitations than usual optical measurements, such as photo-absorption, since it reveals the momentum distribution character related to the initial and final state wavefunctions ($|\psi_i\rangle$ and $|\psi_f\rangle$) [3]. The determination of the wavefunctions of a quantum many-body system, even as simple as a helium atom, is a challenging task, particularly for the excited states. Therefore, the study of the Compton excitation would be of great importance in building the fundamental pictures of quantum mechanics, atoms, molecules and solids.

Although IXS has been known for over forty years, this technique was mostly adopted to the study of condensed matter systems with high density, due to the very small cross section of IXS [4]. For example, IXS has been proved successful in studying charge excitations of superconductors [5], graphite [6], ice [7], and organic molecular crystals [8]. The measurement of Compton excitation on low-density gas phase subject is hampered by the very weak signal that cannot fulfill the high energy resolution requirement ($E/\Delta E \sim 10^5$) of the state-resolved measurement. In recent years, the advance of synchrotron techniques has enabled three pieces of investigation, to the best of our knowledge, on Compton excitations in gases. Žitnik *et al.* reported the Compton excitation spectra in the vicinity of xenon L_3 edge at a scattering angle of 90° with an energy resolution of 1 eV [9]. Kavčič *et al.* reported the spectra of argon gas, where the features related to different two-electron

atomic processes in the vicinity of an inner-shell threshold are separated with an energy resolution of 0.6 eV [10]. Moreover, the Compton excitation spectra for the doubly excited states of helium at three angles were reported by Minzer *et al.* with an energy resolution of 0.9 eV [11]. However, an energy resolutions of 0.6~1 eV of these studies are not enough to resolve the adjacent transitions clearly, especially for excitations of valence shell state in atoms and molecules. Furthermore, there is so far no measurement of the DCS or dynamic structure factor $S(\vec{q}, \omega)$ of Compton excitation for gas phase subject.

In this letter, as the first attempt to measure the state-resolved differential cross sections of Compton excitation for gas phase, we investigated the $S(\vec{q}, \omega)$ of the $1s^2 \ ^1S_0 \rightarrow 1s2s \ ^1S_0$ and $1s^2 \ ^1S_0 \rightarrow 1s2p \ ^1P_1$ transitions of atomic helium with ultra high energy resolution and over a large momentum transfer region by IXS. Spectra have been measured with an energy resolution as high as 70 meV. The selection of helium is because it is the simplest multi-electron system, for which a reliable theoretical calculation can be achieved. Therefore, the $S(\vec{q}, \omega)$ measured with a high resolution would provide a benchmark to test the theoretical method stringently [12, 13]. Historically, helium played an important role in the development of Compton profile since a meaningful comparison between theory and experiment was feasible only on helium atom at that time [14, 15, 16]. Furthermore, the DCS's for $1s^2 \ ^1S_0 \rightarrow 1s2s \ ^1S_0$ and $1s^2 \ ^1S_0 \rightarrow 1s2p \ ^1P_1$ transitions have been studied by the high energy electron-energy-loss spectroscopy (EELS) [17, 18], and the present measurement by IXS provides an independent cross-check.

The present IXS measurements were carried out at the Taiwan Beamline BL12XU of SPring-8 [4]. 3 atm of helium gas was sealed in a gas cell with Kapton windows [Fig. 1(a)]. The energy spread of the incoming beam depends on the monochromator. Two energy resolution setups were exploited. A Si(333) high-resolution monochromator or a Si(400) monochromator is in place to achieve the resolution of 70 meV or 170 meV respectively. Si(555) spherical analyzers with 2 m radius of curvature were used to collect the scattered photons. The analyzer energy for the scattered photon was fixed at 9889.68 eV, while the incident photon energy varied, from which the energy loss is deduced. The momentum resolution is about 0.17\AA^{-1} (or 0.091 a.u. in atomic units). The total absorption of the X-ray is about 13%, which mostly comes from the Kapton window and is constant in the scanned energy range. The scattering signal from the Kapton window is far from the center of gas cell, and is mostly blocked by the post-sample slit. It does contribute to a tiny

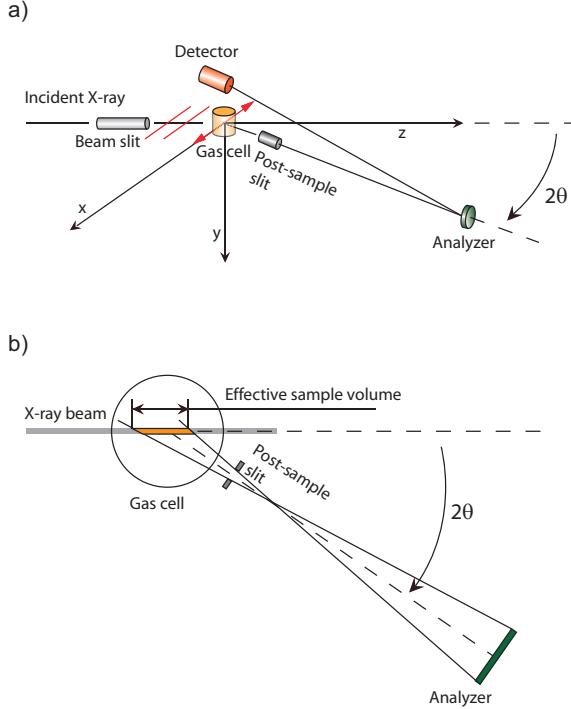


FIG. 1: (color online) (a) Schematics of the experimental setup for inelastic X-ray scattering of gases. The polarization direction of incident photon is along x axis. (b) Deduction of the effective sample volume (top view).

constant background at small 2θ angle region, which can be easily removed during data analysis. The incident beam spot is about $80 \times 120 \mu\text{m}^2$. All of the data were taken at room temperature. As illustrated in Fig. 1(b), the different lengths of the scattering pathway would be detected with varying 2θ , because of the finite size of the gas cell. This leads to an angular factor of $\sin(2\theta)$, which needs to be corrected to extract the DCS of Compton excitation. The fluctuation of the incident X-ray intensity is monitored through a Silicon PIN diode and can be corrected accordingly.

Selected IXS spectra of helium are shown in Fig. 2, and the assignments for the transitions are based on the energy positions of the NIST database [19]. Different from the photo-absorption dominated by the dipolar transition, IXS can excite not only the dipolar transitions but also the transitions of other multipolarity [2, 3, 20]. As a result, the $1s^2$ $^1S_0 \rightarrow 1s2s$ 1S_0 monopolar transition [21] and the $1s^2$ $^1S_0 \rightarrow 1s2p$ 1P_1 dipolar transition are clearly resolved at the present energy resolution of 70 meV, which is the best energy resolution achieved for the gas target of IXS and even slightly better than 80 meV of the

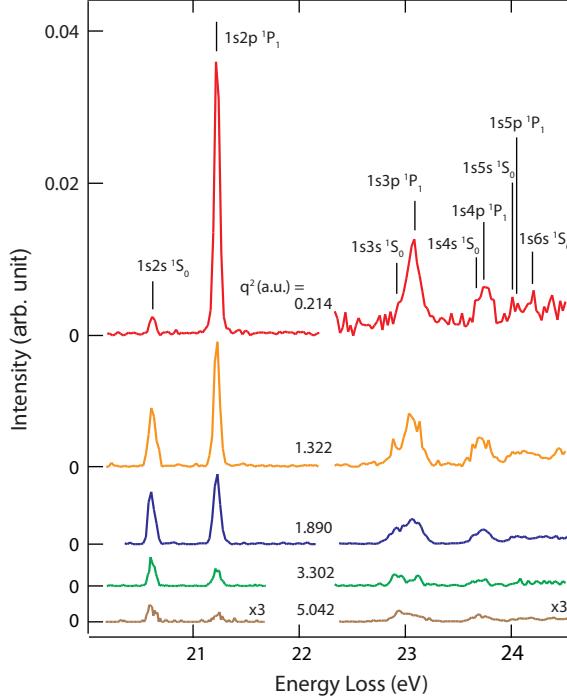


FIG. 2: (color online) Inelastic X-ray scattering spectra of helium gas as a function of energy loss at different momentum transfers, and peaks are labeled by the final state configurations excited from the $1s^2 \ ^1S_0$ ground state. The spectra at lower energy loss range were collected with a resolution of 70 meV, while those at higher energy loss range were gathered with a resolution of 170 meV.

high energy EELS [17, 22]. The measured peak width is limited by the energy resolution. The transitions at higher energy loss range are not clearly resolved due to the limited energy resolution of 170 meV. More detailed information is expected to be revealed with a higher energy resolution in the future. It can also be seen from Fig. 2 that the monopolar transition is much weaker than the dipolar transition at low momentum transfer, while the situation is reversed at high momentum transfer. This illustrates that the dipole approximation for IXS cross section breaks down in the high momentum transfer region [23]. This was reported previously in lithium metal [24], but the current results give a much clearer exemplification of this basic fact of IXS. Similar situation has been observed in high energy EELS experiments before [25].

To determine the DCS's of the $1s^2 \ ^1S_0 \rightarrow 1s2s \ ^1S_0$ and $1s^2 \ ^1S_0 \rightarrow 1s2p \ ^1P_1$ excitations, their respective scattered photon intensities at the energy loss positions of 20.616 eV and 21.218 eV were measured by scanning the scattering angle 2θ from 5° to 60° . To calibrate

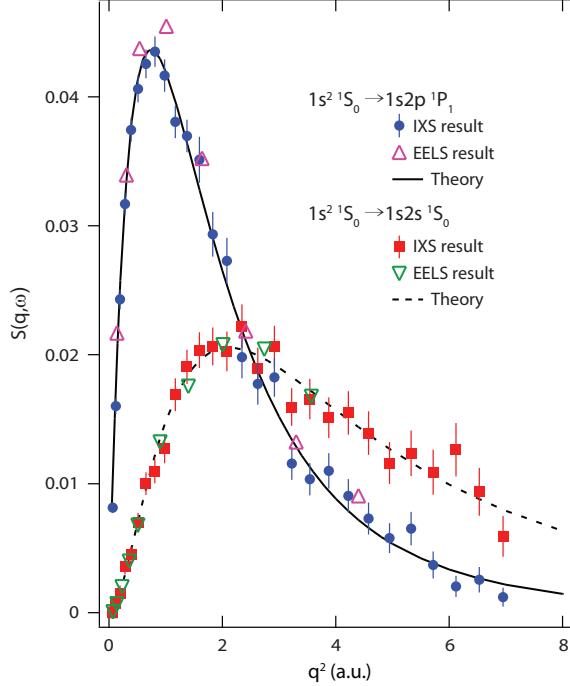


FIG. 3: (color online) The dynamic structure factor $S(\vec{q}, \omega)$ of the $1s^2 \ ^1S_0 \rightarrow 1s2s \ ^1S_0$ monopolar transition and the $1s^2 \ ^1S_0 \rightarrow 1s2p \ ^1P_1$ dipolar transition of helium measured by IXS. The high energy EELS data [17, 18] and the theoretical calculations [13] were converted from the generalized oscillator strengths. Data were taken with 170 meV resolution. Note the horizontal axis is $q^2 = k_i^2 + k_f^2 - 2k_i k_f \cos(2\theta)$, following the convention in atomic physics.

the background, a 2θ scan was run at 20.1 eV energy loss, since it is in a flat and featureless region of the IXS spectrum [Fig. 2]. After correcting the contribution of background and effective scattering volume at different scattering angles [Fig. 1(b)], the dynamic structure factor $S(\vec{q}, \omega)$ for these two transitions were obtained via dividing the DCS's by the factor of $\cos^2(2\theta)\omega_f/\omega_i$ for the incident photon polarization in the scattering plane, and scaling the value of $1s^2 \ ^1S_0 \rightarrow 1s2p \ ^1P_1$ transition to the theoretical one at $q^2 = 0.81$ a.u. Fig. 3 shows the measured dynamic structure factor $S(\vec{q}, \omega)$ of the monopolar excitation of $1s^2 \ ^1S_0 \rightarrow 1s2s \ ^1S_0$ and the dipolar one of $1s^2 \ ^1S_0 \rightarrow 1s2p \ ^1P_1$ along with some previous high energy EELS data [17, 18]. Theoretical calculations based on the explicitly correlated wave functions are also presented [13]. Compared with the commonly used Hylleraas-type wave functions, Cann and Thakkar used the exponential correlation factors to describe the electron correlations in their calculation, and the calculated energies are in agreement with the best published values within nanohartrees [13]. It can be seen from Fig. 3 that the almost perfect match of

the theoretical curves with the present data in a broader momentum range confirms that the calculated wave functions is close to the actual wave functions to a great detail in real space. It can also be noticed that the $S(\vec{q}, \omega)$ for the dipole excitation is concentrated in the low momentum transfer, while that for the monopole excitation is much broader in momentum space. This can be reasonably explained by the fact that the wave function of $1s2p\ ^1P_1$ is more extended in real space than that of $1s2s\ ^1S_0$.

It is worth noting that IXS and high energy EELS are complementary. Measuring $S(\vec{q}, \omega)$ by these two independent techniques provides a means of data cross-check. Because the extraction of $S(\vec{q}, \omega)$ from high energy EELS data is based on the validity of the first Born approximation (FBA), which requires a high incident electron energy [20]. As for how high the incident energy has to be, it can only be determined on a trial-and-error basis. However, IXS is more straightforward [2], so that its cross section can serve as a benchmark to test whether the FBA holds in EELS experiments. Moreover, high energy EELS has much larger cross sections than IXS for the lower momentum transfer. However, this cross-section advantage of the electron scattering method rapidly diminishes with a rate of q^{-4} (Rutherford cross section) as the momentum transfer increases, while the cross section of Compton scattering is simply proportional to $S(\vec{q}, \omega)$. It is also known that high energy EELS suffers from multiple scattering at high q , while the IXS does not. Generally speaking, high energy EELS is more effective to study the large-scale structures of wavefunctions (lower q), while IXS is reliable at all length scales. As a result, the collection of IXS data presented in Fig. 3 over such a broad momentum range only takes several hours, while the high energy EELS data requires several weeks. Since the pressure in the gas cell could be further increased, there is a tremendous potential for IXS in studying the excitations of atoms and molecules.

Practically, IXS could be readily extended to more applied research where the gas systems may be subject to various extreme physical and chemical conditions, such as in catalysis, and under extreme pressure and temperature conditions. The IXS data may be used, for example, to identify chemical species *in situ* as they are produced. This type of experimental environments is beyond the reach of other experimental techniques such as EELS and photoemission.

In conclusion, we have demonstrated that IXS is a powerful tool to study the excitations in atomic or molecular systems at a third generation synchrotron. The dynamic structure factors of the $1s^2\ ^1S_0 \rightarrow 1s2s\ ^1S_0$ monopolar excitation and the $1s^2\ ^1S_0 \rightarrow 1s2p\ ^1P_1$ dipolar

excitation of atomic helium have been measured by the high-resolution IXS over a wide momentum transfer range. The almost perfect match of the present measurement with the theoretical calculations gives a rigorous test of the theoretical method, and demonstrates the cleanliness of the data. Furthermore, our data provide a benchmark for the direct determination of the absolute DCS values of other gases in future experiments, e.g., with a mixed-gas setup.

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